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Chemistry at the Limits of Coordination

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High coordination anion chemistry has developed rapidly in the last decade most notably in the field of binary fluorides. The discovery of a truly anhydrous fluoride source, tetramethylammonium fluoride, $(\text{CH}_3)_4\text{NF}^1$, has led to a renaissance in main group chemistry. Tetramethylammonium fluoride is thermally stable, soluble in organic solvents, and surprisingly resistant to powerful oxidizers such as ClF_3 , BrF_5 , and IF_7 . Many new anions have been synthesized and characterized through the use of this fluoride source.²⁻⁶ However, relatively few dianions have been studied and characterized to date, including XeF_8^{2-} ⁷⁻¹⁰, TeOF_6^{2-} ⁴, TeF_8^{2-} ⁵, and MF_5^{2-} ($\text{M} = \text{As}, \text{Sb}, \text{Bi}$)¹¹. Problems plaguing the study of new dianions include poor solubility in solution, and the equilibrium between the dianion and its monoanion and fluoride precursors. Several new fluorodianions have been synthesized, characterized through vibrational spectroscopy, and compared to theoretical calculations.

The reinvestigation of an original sample of " Cs_3IF_6 "¹² found strong evidence that the sample is actually a mixture of Cs_2IF_5 and CsF rather than Cs_3IF_6 . This conclusion has been drawn from the fact that the sample had a Raman band pattern very similar to that reported for the recent, structurally characterized XeF_5^- ¹³. The infrared spectrum and x-ray powder spectrum of " Cs_3IF_6 " contained bands indicative of large amounts of CsF .

The IF_5^{2-} dianion can also be formed in acetonitrile at low temperatures through the reaction of tetramethylammonium fluoride and IF_3 . It can be made either stepwise through the well known IF_4^- , or by the reaction of two equivalents of tetramethylammonium fluoride with IF_3 . Theoretical calculations were carried out at the SCF/ECP level of theory where a minimum was found for the pentagonal planar D_{5h} structure. The observed vibrational spectra are in excellent agreement with those calculated for pentagonal planar IF_5^{2-} and with those found for isoelectronic, pentagonal planar XeF_5^- .

The IF_7^{2-} dianion has been prepared by several routes in our laboratory. Two routes involve vacuum pyrolyses, which were carried out in sapphire tube reactors. It was first found that heating a mixture of $\text{KIF}_6 \cdot n\text{IF}_7$ resulted in the formation of K_2IF_7 with IF_7 and IF_5 . Later, it was found that heating pure KIF_6 led to K_2IF_7 and IF_5 . The IF_7^{2-} dianion can also be synthesized through the reaction of $(\text{CH}_3)_4\text{NF}$ with IF_5 in acetonitrile at room temperature. The vibrational spectra of K_2IF_7 are very similar to those of the structurally characterized and isoelectronic CsXeF_7^{14} , indicating the same C_{3v} monocapped octahedral structure.

Presently, there are no nine-coordinate main group AX_9 species known. Theoretical calculations for IF_9^{2-} show that a slightly distorted D_{3h} structure is vibrationally stable. This structure is very reminiscent of the well known ReH_9^{2-15} structure. To date, laboratory efforts have not been successful. The reaction of either two or three equivalents of CsF with IF_7 at high temperatures in a monel cylinder under a fluorine

atmosphere has failed. The reactions of $(\text{CH}_3)_4\text{NF}$ with IF_7 in cold acetonitrile, either stepwise through IF_8^{2-} , or all at once, also were unsuccessful.

SbF_5 and BiF_5 are strong Lewis acids which react quantitatively with a fluoride ion source forming the well known octahedral SbF_6^- and BiF_6^- species. From the known existence of TeF_8^{2-} ^{4, 16-17}, whose precursor TeF_6 has a similar fluoride affinity as BiF_5 ¹⁸, the formation of SbF_7^{2-} and BiF_7^{2-} through the reaction of excess CsF with the corresponding Lewis acid seemed reasonable. In the case of SbF_5 , only partial conversion to SbF_7^{2-} was achieved with a 2:1 CsF/SbF_5 reaction mixture. Even using a 3:1 CsF/SbF_5 ratio, the product still contained some CsSbF_6 . For Bismuth, it was found that a 2:1 ratio of CsF/BiF_5 gave a high conversion to Cs_2BiF_7 , but there was still some CsBiF_6 present. The Raman signals due to BiF_6^- diminished by raising the temperature of the reaction to 300 °C. Bismuth pentafluoride reacted smoothly with $(\text{CH}_3)_4\text{NF}$ at low temperatures in acetonitrile to form the BiF_7^{2-} dianion. In the case of SbF_5 , reaction with a large excess of $(\text{CH}_3)_4\text{NF}$ in acetonitrile or sulfur dioxide, gave exclusively the SbF_6^- anion. The vibrational frequencies for the SbF_7^{2-} dianion were calculated at the SCF/ECP level of theory with a minimum being found for the pentagonal bipyramidal D_{5h} structure. The calculated frequencies and intensities agreed well with the ones found for Cs_2SbF_7 . The vibrational frequencies for the BiF_7^{2-} dianion were calculated at the HF level of theory using DZP(F) and ECP/DZP(Bi) basis sets, which also found a minimum for the pentagonal bipyramidal D_{5h} structure. Again, the calculated frequencies and intensities agreed well with the observed ones.

In summary, several new doubly charged anions, IF_5^{2-} , IF_7^{2-} , SbF_7^{2-} , and BiF_7^{2-} have been prepared and characterized. IF_5^{2-} and IF_7^{2-} are only the second known examples of a pentagonal planar AX_5E_2 and a monocapped octahedral main group AX_7E species, respectively. BiF_7^{2-} and SbF_7^{2-} are the first examples of seven coordinate AX_7 pnictogens, and both dianions adopt a pentagonal bipyramidal structure.

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